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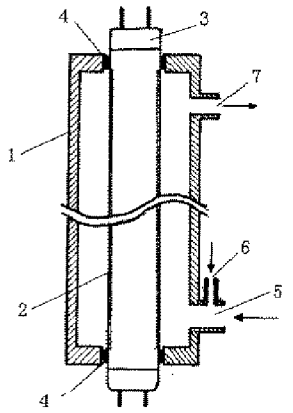
CLAIM + DETAILED DESCRIPTION

[Claim(s)]
[Claim 1]
A photocatalyst which consists of fused silica which carried out halide acid treatment.
[Claim 2]
The photocatalyst according to claim 1 whose halide acid is hydrofluoric acid.
[Claim 3]
A detoxication disposal method of quality of noxious organic substances making a photocatalyst which consists of fused silica which carried out halide acid treatment contact, irradiating a mixture of quality of noxious organic substances, and oxygen with radiation, and carrying out a photolysis.
[Claim 4]
A detoxication disposal method of the quality of noxious organic substances according to claim 3 whose toxic substance is an organic halogenated compound.

[Detailed Description of the Invention]
[0001]
[Field of the Invention]
This invention induces the synchrotron orbital radiation covering a large wavelength area, and relates to the detoxication disposal method of the new photocatalyst for carrying out the photolysis of the quality of noxious organic substances, and detoxicating it effectively, and the quality of noxious organic substances using it.
[0002]
[Description of the Prior Art]
Usually, by making the catalyst which produces an electronic excited state for the reaction which does not advance if very high energy is not given by light exist, generally the reaction advanced with very low energy is called photocatalysis, and the catalyst used in this case is called photocatalyst.
[0003]
Although what is called a semiconductor catalyst of titanium oxide, zinc oxide, cadmium sulfide, tungstic oxide, etc. and a metal complex catalyst like a ruthenium bipyridyl complex are known until now, [as this photocatalyst] Since titanium oxide is the most extremely stable in these and living thing toxicity is

Drawing selection
Drawing 1



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moreover hardly shown, it is widely used as various kinds of chemical reactions and a photocatalyst for an environmental clean-up.

[0004]

In the charge site which produced charge separation, was carried out in this way and produced when the electron in a filled band was excited by the conduction band by the exposure of the near-ultraviolet light near 400 nm, [this titanium oxide] A hydroxyl radical and a superoxide anion occur and an organic halogenated compound and an environmental pollutant like NOx are disassembled in these powerful oxidation operations.

[0005]

However, it is only a wavelength band near 400 nm that titanium oxide can demonstrate photocatalyst ability, and it does not act as a photocatalyst in the other wavelength band. This is the same also about photocatalysts other than titanium oxide, and shows a catalysis only in the optical absorption field of itself. Therefore, the photocatalyst for decomposing the quality of noxious organic substances known until now has the low utilization efficiency over the light covering a large wavelength area like sunlight, and does not escape that the use range is restricted.

[0006]

On the other hand, although using silica as a photocatalyst is also known, [the method (refer to nonpatent literature 2) of carrying out epoxidation of the propene by gas-like oxygen under existence of the method (refer to nonpatent literature 1) of photooxidizing ethylene, using silica as a catalyst, silica, or manganese support silica, etc.] The reaction in these methods advanced for the first time, using a very-high-pressure mercury lamp as a light source, and also its conversion rate was also as low as 28.9%, and it was not able to say the method it may not necessarily be satisfied with putting in practical use of the method.

[0007]

[Nonpatent literature 1]

"SUTADEIZU yne surface science and KYATARISUTSU (Studies in Surface Science and Catalysts)", the 130th volume, 2000, p.1955-1960

[Nonpatent literature 2]

"Journal OBU KYATARISUTSU (J. Catalysts)", the 171st volume, 1997, p.351-357

[0008]

[Problem to be solved by the invention]

The optical absorption to sunlight is hardly accepted, but this invention is made for the purpose of providing the photocatalyst which may decompose the quality of noxious organic substances which causes environmental pollution with high utilization efficiency in a large wavelength area.

[0009]

[Means for solving problem]

The result of having repeated research wholeheartedly in order that this invention persons might develop the new photocatalyst which acts on the synchrotron orbital radiation covering a large wavelength area, If the fused silica which did not attract attention at all as a photocatalyst until now is processed with halide acid, the operation as a photocatalyst will be produced, And the thing for which high utilization efficiency is shown to the synchrotron orbital radiation covering the large wavelength area ranging from ultra-violet to a visible portion also unexpectedly like sunlight, And if this photocatalyst is used, it will find out that the various quality of noxious organic substances constituting the main causes of environmental pollution is decomposed, and it can detoxicate, and based on this knowledge, it came to make this invention.

[0010]

That is, this invention is contacted to this photocatalyst, irradiating with radiation the mixture of the photocatalyst which consists of fused silica which carried out halide acid treatment and the quality of noxious organic substances, and oxygen, and provides the detoxication disposal method of the quality of noxious organic substances carrying out a photolysis.

[0011]

[Mode for carrying out the invention]

Although the photocatalyst of this invention is constituted as a subject, [a photocatalyst] [on substance] [the fused silica which carried out halide acid treatment] This fused silica is transparent melting glass which carries out melting, solidifies under the conditions strictly controlled so that impure part concentration was set to 50 ppm or less by using the source of a silicon oxide, for example, quartz, and quartz sand of natural origin as a raw material, and is obtained. This thing has the purity more than $SiO_2$99.995 mass %, and, [as non-purity] For example, less than aluminum:14ppm, As : 0.1 ppm or less, B:0.2 ppm or less, Ca: Less than 0.6ppm, less than Cd:0.01ppm, Cr : 0.05 ppm or less, Cu: Less than

0.05ppm, Fe : 0.5 ppm or less, K:0.6 ppm or less, Li: Less than 0.6ppm, less than Mg:0.1ppm, less than Mn:0.7ppm, less than Na:0.7ppm, less than nickel:0.1ppm, P:0.2 ppm or less, less than Sb:0.003ppm, less than Ti:500ppm, Zr: 0.8 ppm or less etc. are included. This thing shows strong absorption of OH kind in infrared-absorption-spectrum analysis.
Such fused silica is marketed from the general electric company (GE) as product name quartz watch GE124, 144, 214, 219, 224, 254, etc.
[0012]
Next, halide acid treatment of this fused silica is performed by carrying out flush desiccation, for example, after fused silica is immersed in a halide acid aqueous solution. Under the present circumstances, as halide acid to be used, although there are hydrofluoric acid, hydrochloric acid, hydrobromic acid, etc., for example, especially hydrofluoric acid is preferred. these halide acid -- 1 - 50 mass % concentration -- it is preferably used as an aqueous solution of 5 - 20 mass % concentration. As long as the time which this halide acid treatment takes changes with the kind of halide acid to be used, and the concentration in that aqueous solution and a high-concentration aqueous solution is generally used for it, a short time may be sufficient as it, if a low-concentration aqueous solution is used, it will require a long time, but it is usually chosen in the range for 5 to 60 minutes.
[0013]
Thus, the photocatalyst of this invention obtained is a dense solid after the density 2.2 - 2.3 g/cm^{3}g, and tabular, grain form, powder, the shape of a block, fibrous, etc. can make the shape form arbitrarily according to a request.
[0014]
Although the photocatalyst of this invention has the operation which decomposes the quality of noxious organic substances by the exposure of radiation, [a photocatalyst] Although trichloroethylene, tetrachloroethylene, dichlorodifluoromethane, tribromomethane, and the organic halogenated compound leading to environmental pollution like polychlorobiphenyl (PCB) can be mentioned especially as this quality of noxious organic substances, In addition, it is effective also to an aromatic compound like toluene and xylene, the aldehyde like formaldehyde and acetaldehyde, a sulphur-containing compound like ethanedithiol, etc.
[0015]
Oxygen is mixed in the quality of noxious organic substances, and a photocatalyst is made to contact, in order to decompose and detoxicate the quality of noxious organic substances using the photocatalyst of this invention, irradiating this mixture with synchrotron orbital radiation.
Although a semiconductor photocatalyst like old TiO_2 or ZnO shows the decomposition capability, [a semiconductor photocatalyst] [only in the optical absorption field of the quality of noxious organic substances] In the light of the other wavelength, in order not to demonstrate catalyst capability, when natural light like sunlight is used, do not escape that the utilization efficiency of light becomes low, but, [the photocatalyst of this invention] Since the light of the wavelength which hardly shows optical absorption can also decompose the quality of noxious organic substances, the synchrotron orbital radiation of a wide range wavelength area, for example, ultraviolet radiation and visible light, can be used.
[0016]
That is, the wavelength area of ultraviolet radiation can use the synchrotron orbital radiation of a wavelength area [photocatalyst / of this invention] as wide range as 200-800 nm, although the wavelength area of 200-400 nm and visible light is considered to be 400-800 nm. When it is efficient and makes an organic halogenated compound disassemble, it is preferred to use the synchrotron orbital radiation of a 240-500-nm wavelength area.
[0017]
As a light source made to generate these synchrotron orbital radiation artificially, an ultraviolet ray lamp, a xenon lamp, a fluorescent lamp, an incandescent lamp, etc. which are commonly used, for example as a source of synchrotron orbital radiation can be mentioned.
[0018]
When performing the photolysis of the quality of noxious organic substances continuously using the photocatalyst of this invention, this quality of noxious organic substances is made to **** into a fluid, for example, a gas, or a fluid with oxygen, and a photocatalyst is made to contact, but as a fluid used in this case, unless the photolysis of the quality of noxious organic substances is checked, there is no restriction. However, it is available in large quantities and water is preferred as nitrogen gas and a fluid as a gas at the point of not becoming a cause of environmental pollution.
[0019]

[on the occasion of the photolysis of the quality of noxious organic substances] [oxygen concentration / of the fluid which this is made to mix] Since it is so preferred that this concentration is large although there is no restriction in particular since the decomposition efficiency of the quality of noxious organic substances becomes high, but it is preferred to use air a cost field when a fluid is a gas, Since oxygen concentration becomes about 20 volume % and water is used for the same Reason in the case of a fluid, oxygen concentration becomes 4.9 volume % (standard state).
on the other hand -- as opposed to one carbon atom contained in the molecule of the quality of noxious organic substances if oxygen to the quality of noxious organic substances carries out comparatively -- an oxygen molecule -- even if small, two rates are preferred, but there is no restriction in particular.
[0020]
[in this invention method] [as a method of contacting the mixture of the quality of noxious organic substances, and oxygen to a photocatalyst] Both can be sealed hermetically in a well-closed container and all of a flow method to which the batch method and fluid in which a fluid and the photocatalyst surface are contacted by the thermal motion of a fluid are made to flow compulsorily, and a fluid and the photocatalyst surface are contacted can be used.
[0021]
Next, how to carry out the photolysis of the quality of noxious organic substances, and detoxicate it using a photocatalyst, according to an accompanying drawing, is explained.
Drawing 1 is a longitudinal section showing one example of a suitable device to enforce this invention method, In the glass cylindrical well-closed container 1, the low pressure mercury lamp 3 made into the overcoat is arranged [photocatalyst / 2 /, i.e., the formless quartz glass pipe which carried out halide acid treatment,] in the surface, and these both ends have the end 4 of the well-closed container 1, and the structure supported by 4'.
[0022]
After a fluid, i.e., a gas, or a fluid ****, flowing in the well-closed container 1 from the feed hopper 5, being mixed with the oxygen introduced from the oxygen feed port 6 and the quality of noxious organic substances contacting the photocatalyst 2, it is discharged from the outlet 7 outside. In the meantime, the mixture of the quality of noxious organic substances and oxygen receives the exposure of the synchrotron orbital radiation from the low pressure mercury lamp 3, a photolysis advances, and detoxication is performed.
[0023]
After this device supplies the fluid which contained the quality of noxious organic substances, and oxygen in the packed bed of silica provided with the window of quartz for an exposure of light, or quartz glass from the feed hopper 5 and contacts this packed bed and a fluid, it can also be made into the structure which may flow out of the outlet 7. As a feeding method of the fluid in this device, although the method of forming a pressurization pump in the entrance side or the method of forming a decompression pump in an outlet side is common, other fluid supply methods, such as a blowing method by the fan in the case of a gas and the gravity flowing-down method in the case of a fluid, can be used.
[0024]
The size of a packed bed and the rate of flow of a fluid are decided by concentration of the quality of noxious organic substances and irradiation light intensity, processing unit structure, etc. to process, and a specific numerical value cannot prescribe them. If it puts in another way, what is necessary will be just to set up the operating condition that the nature concentration of noxious organic substances in the fluid which carried out photolysis treatment is hardly detected.
[0025]
As a light source in this device, when the quality of noxious organic substances contacts the photocatalyst surface, the irradiation light intensity into which this substance may be made to disassemble can be generated, and there should just be no restriction in particular. As such a thing, sunlight irradiation equipment can be mentioned for the usual ultraviolet ray lamp, xenon lamp, fluorescent lamp, and incandescent lamp as natural light equipment as artificial light equipment again.
[0026]
Drawing 2 is a longitudinal section showing one example of the device used when a batch method performs, Enclose the mixture of the quality of noxious organic substances, and oxygen from the gas inlet 9 provided with the valve into the well-closed container 1 provided with the window 8 for light irradiation (it isolates with the exterior with quartz or quartz glass) which inserted in the photocatalyst 2, and it lets the window 8 for light irradiation pass, After irradiating with synchrotron orbital radiation until the quality of noxious organic substances disappears, the gas containing a decomposition product is taken out from the

gas exhaust 10 provided with the valve. Detoxication can be attained easily, without performing excessive operation, if it does in this way. The above-mentioned window 8 for light irradiation can be made to form in arbitrary shape, such as planate, curved surface shape, and the shape of a cylinder.

[0027]

Since it can be produced by low cost since this device should just be a well-closed container which has a portion which has a window of quartz in which light irradiation is possible, or the product made from quartz glass, and holds a photocatalyst inside, and it can use sunlight, it can also make running cost low.

[0028]

As mentioned above, even if it uses which device, about the temperature which reacts, there is no restriction in particular and it can choose arbitrarily within the limits of -30 to 550 **. Although this decomposition reaction advances enough under an atmospheric pressure, if it is a request, it can be pressurized and can also promote a reaction.

Thus, 100% of a decomposition rate can be attained under light intensity 0.1 - 1.0 mW/cm^2, and the conditions for irradiation time 40 to 360 minutes.

[0029]

[Working example]

Next, although an embodiment explains this invention still in detail, this invention is not limited at all by these.

[0030]

The experiment of each embodiment was conducted using the reactor shown in drawing 3 by operating it according to an order of following (a) thru/or (i).

[0031]

(a) Set sample pan SP who put the catalyst sample CS so that the window W for light-receiving in the reaction vessel R might be coincided.

[0032]

(b) Drive vacuum pump P and open the method cock C1 of two, and C2. The three way stop cock CT is opened so that the cock C2 and the pressure sensing machine G may be in switch-on. And gas (residual air) which exists between three way stop cock CT1 and the pressure sensing machine G from the method cock C1 of two is exhausted.

[0033]

(c) When a directions value of the pressure sensing machine G is set to 1.0 or less Torr, close the cock C1.

[0034]

(d) Set massflow controller FC1 for oxygen gas supply as 20 ml/min, and set massflow controller FC2 for nitrogen gas supplying as 80 ml/min, make it drive and. The three way stop cocks CT1 and CT2 are made into switch-on so that those gas can be introduced to the reaction vessel R.

[0035]

(e) When mixed gas of oxygen and nitrogen is supplied to the reaction vessel R via the mixed gas reservoir machine MR and a directions value of the pressure sensing machine G reaches atmospheric pressure power, intercept the three way stop cocks' CT1 and CT2 switch-on.

[0036]

Gas exchange (exhaust air and supply) operation in the reaction vessel R of (e) is repeated 3 times from (f) and (b). If the reaction vessel R is filled up with oxygen gas and nitrogen gas at the 4th time, the method cocks C1 and C2 of two will be closed. And vacuum pump P and the massflow controllers FC1 and FC2 are suspended.

[0037]

(g) Pour in about 1.0micro of organic substances (example: trichloroethylene) l from the reactant gas extraction mouth E by a syringe, and carry out 1hr maintenance. When 1hr progress was carried out, 1.0 ml of filler gas in the reaction vessel R was extracted from the reactant gas re-extraction mouth E, the gas concentration was measured by GASUKURO, and it was considered as the initial fill ration of the organic substance.

[0038]

(h) Turn on the light source LS (example: low pressure mercury lamp), and apply the irradiation light LB to the catalyst sample CS through the window W for light-receiving.

[0039]

(i) 1.0 ml of gas after predetermined time light irradiation and in the reaction vessel R was extracted, it asked for the residual concentration of the organic substance by GASUKURO, and quantity which decreased from the initial fill ration was made into the amount of decomposition.

In the inside H of a figure, the fringe of a reaction vessel and the clasp of a lid are shown.

[0040]

Reference example 1

2 l. of hydrogen fluoride aqueous solutions of 10 mass % concentration are accommodated in a 3-l. volume polyethylene container, It took out, after immersing the cylinder tube made from fused silica (product [made by GE], and product name "quartz watch GE214" density 2.21 g/cm^3) and shaking for 10 minutes in 25 ** into this, and it washed, and the cylindrical photocatalyst was manufactured by drying. The total surface area of this photocatalyst was 1.4x10 ^{2}cm^2.

[0041]

Reference example 2

After immersing the same cylinder tube made from fused silica as having used by the reference example 1 in the hydrogen chloride aqueous solution of 3 molar concentration (11.0 mass %) and shaking for 60 minutes in 25 **, it washed and the cylindrical photocatalyst was manufactured by drying. The total surface area of this photocatalyst was 1.4x10 ^{2}cm^2.

[0042]

EXAMPLE

The photocatalyst manufactured by the reference example 1 or 2 inside the cylindrical reaction vessel (45 mm in inside diameter and 200 mm in length) is arranged, Toluene (TLE), acetaldehyde (ALD), ethanedithiol (ETL), or trichloroethylene (TCE) is enclosed with this with dry air (O_2/N_2 volume ratio = 1/4), The photolysis of the synchrotron orbital radiation was irradiated with and carried out by the irradiation time shown in Table 1 in 24 **, using a low pressure mercury lamp (light intensity 0.15 mW/cm^2 in line special light source UVL-10, the wavelength of not less than 230 nm, and the sample surface) as a light source. The result is shown in Table 1. The result at the time of using a commercial photocatalyst (TiO_2) for comparison was also written together.

[0043]

[Table 1]

光触媒		照射条件		有機物質				単位時間、単位面積当りの分解速度
種類	全表面積 (cm^2)	時間 (分)	強度 (mW/cm^2)	種類	気相中濃度(μmol) 充填量	分解量	分解率 (%)	(μmol/分・cm^2)
参考例1	1.4×10^2	880	0.15	TLE	9.4	2.56	27	2.1×10^{-5}
参考例1	1.4×10^2	1160	0.15	ALD	15	5.2	35	3.2×10^{-5}
参考例1	1.4×10^2	120	0.15	ETL	9.5	6	63	3.5×10^{-4}
参考例1	1.4×10^2	210	0.15	TCE	1.3	0.32	24	1.7×10^{-5}
参考例1	1.4×10^2	110	0.15	TCE	1.1	1.1	100	7.1×10^{-5}
参考例1	1.4×10^2	150	0.15	TCE	1.2	1.2	100	5.7×10^{-5}
参考例1	1.4×10^2	120	0.15	TCE	1.2	1.2	100	7.1×10^{-5}
参考例1	1.4×10^2	60	0.15	TCE	1.8	1.8	100	2.1×10^{-4}
参考例2	1.4×10^2	180	0.15	TCE	1.3	1.3	100	5.2×10^{-5}
参考例1	1.4×10^2	*510	0.19	TCE	8.9	0.77	8.6	1.1×10^{-5}
市販光触媒	4.5×10^5	150	0.15	TCE	0.58	0.58	100	8.3×10^{-9}

* : the black light (light intensity ^{2} of 0.19mW/cm on national FL6BL, 6W, and the surface of a sample) was used as a light source.

[0044]

If the photocatalyst of this invention is used as shown in this table, compared with the case where the TiO_2 photocatalyst currently conventionally used widely is used, no less than 4-5 figures can carry out the photolysis of the various quality of noxious organic substances with quick catabolic rate.

[0045]

[Effect of the Invention]

In this invention, the new photocatalyst which consists of fused silica by which hydrogen halide treatment was carried out and which was not known until now is used.

Therefore, while being known until now, decomposition removal of the quality of noxious organic substances can be carried out at the decomposition rate which is equal to the titanium oxide catalyst used as the most outstanding photocatalyst.

[Brief Description of the Drawings]
[Drawing 1]The longitudinal section showing the example of a device for carrying out the photolysis of the quality of noxious organic substances continuously using this invention photocatalyst.
[Drawing 2]The longitudinal section showing the example of a device for carrying out the photolysis of the quality of noxious organic substances by a batch type using this invention photocatalyst.
[Drawing 3]The explanatory view of the reactor used in the embodiment.
[Explanations of letters or numerals]
1 Well-closed container
2 Photocatalyst
3 Light source
5 Fluid feed hopper
6 Oxygen feed port
7 Outlet
8 Window for light irradiation
9 Gas inlet
10 Gas exhaust
R Reaction vessel (with a cover)
W The window for light-receiving
CS Catalyst sample
SP Sample pan
P Vacuum pump
C1 and C2 Method cock of two
CT1, CT2 three way stop cock
G Pressure sensing machine
FC1 and FC2 Massflow controller
MR mixed gas reservoir machine
E Reactant gas extraction mouth
LS Light source
LB Irradiation light
The fringe of H reaction vessel, and the clasp of a lid

[Translation done.]